Pine River DDT Sediment Site – A Nonattenuation Site

James Chapman, Ph.D.
Ecologist
USEPA Region 5

Site History

- 50-acre chemical plant at located at St. Louis, Gratiot Co., MI
  - Adjacent to Pine River Impoundment formed by the St. Louis dam
- 1936–1976 Michigan Chemical Corp.
- 1976-1978 (closed) Velsicol Corp.

1982 Consent Judgment

- Main Chemicals of Concern
  - PBB – polybrominated biphenyl
  - DDT – 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
  - HBB – hexabromobenzene
  - Tris – tris(2,3 dibromopropyl)phosphate
- Remediate main plant site
  - Demolish buildings
  - Clay cap
  - Containment wall to prevent further contamination of the Pine River impoundment

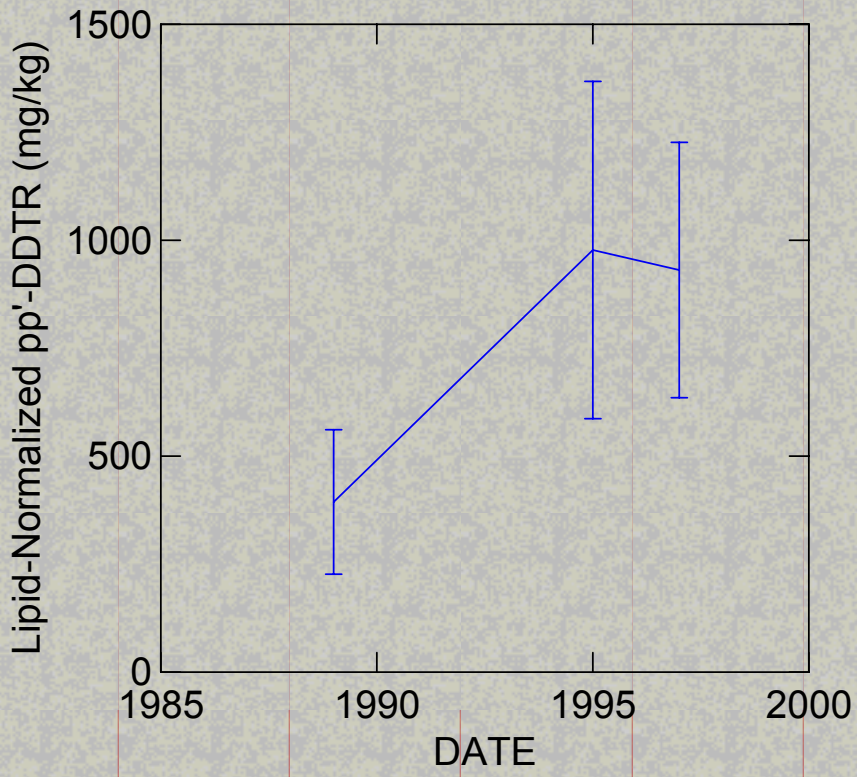
1982 Consent Judgment

- “Following analysis of the relevant environmental conditions, the parties have concluded that the most appropriate environmental alternative for the Pine River/St. Louis Reservoir sediments is to leave the existing contaminated sediments undisturbed.”
- MI is responsible for fish monitoring

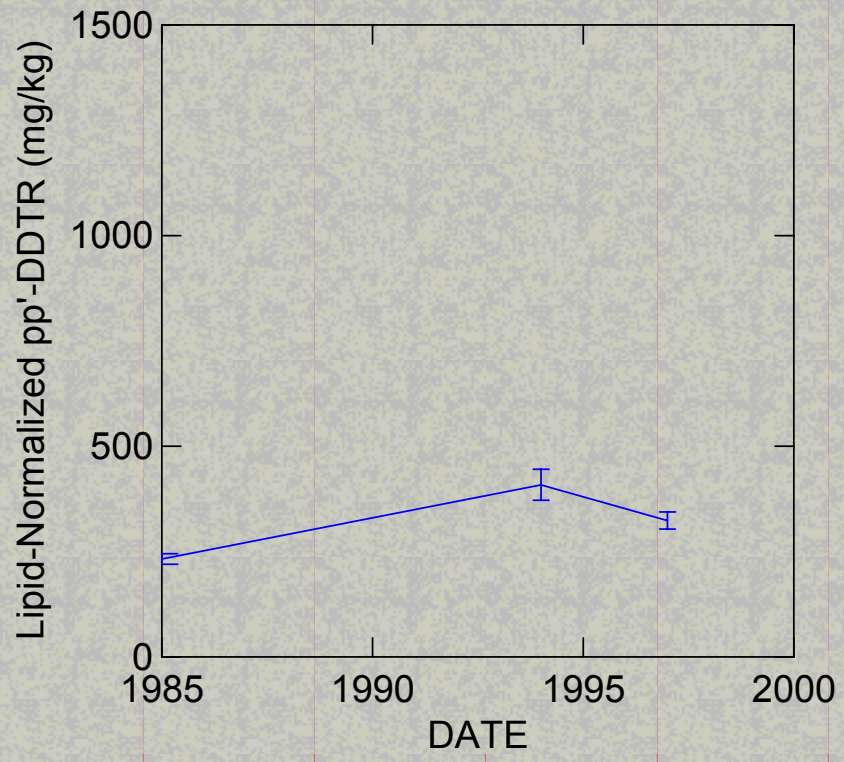
Nonattenuation

- Contrary to expectations, lipid-normalized pp-DDTR (pp-DDT, pp-DDE, and pp-DDD) conc. in carp skin-off fillets **increased** over time.
  - + 140-150 % in the St. Louis impoundment
    - 1989 to 1995/1997
  - + 40-80 % downstream of the dam
    - 1985 to 1994/97

Carp Fillet Monitoring Data, St. Louis Impoundment (+/- SEM)



Carp Fillet Monitoring Data, Downstream of St. Louis (+/- SEM)



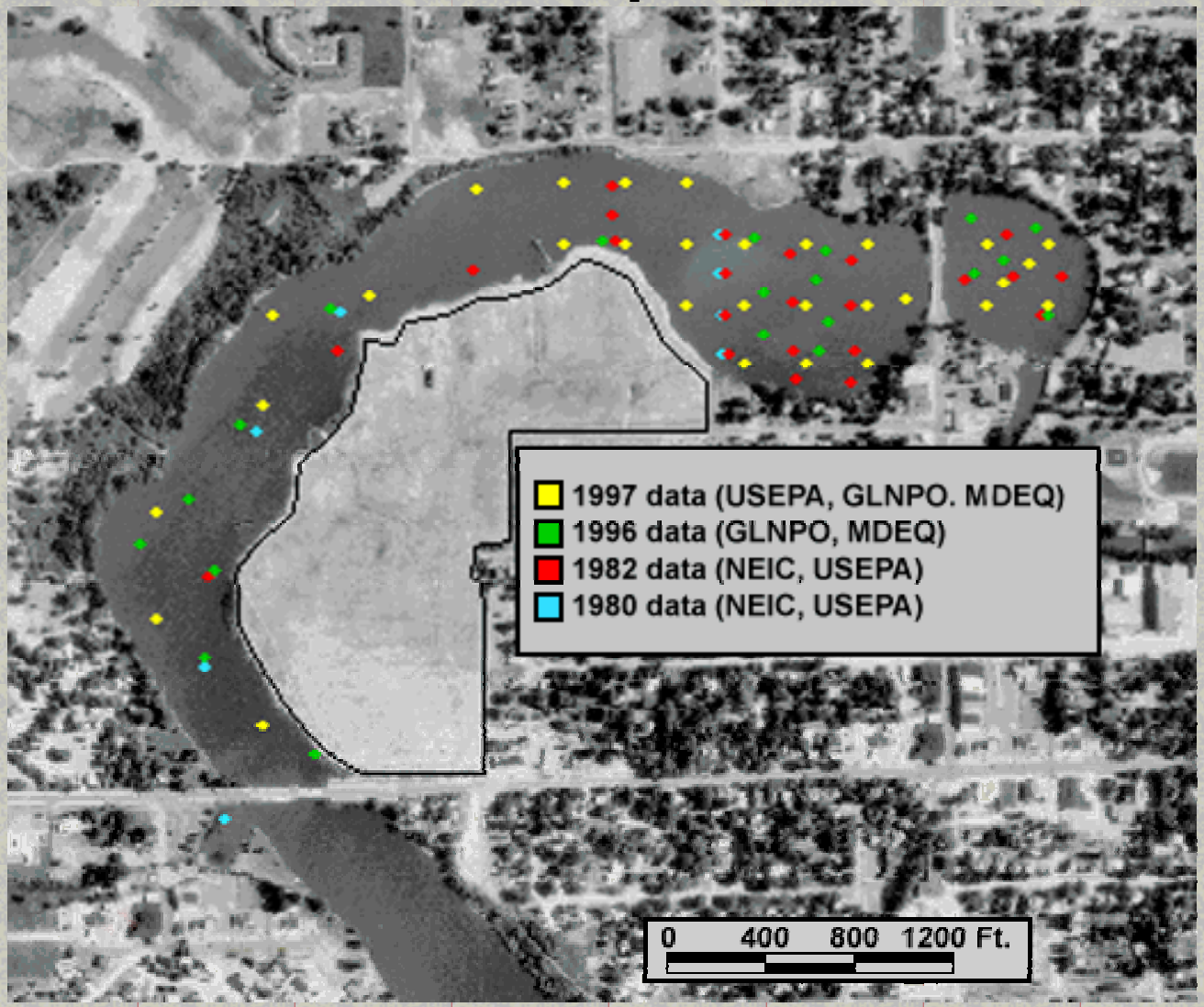
Biological Half-life in Fish

- Total DDT
  - 64-428 days (menhaden)
  - No apparent elimination in 1 study (trout)
- pp'-DDE
  - 336 d (trout)
    - Niimi, A. 1987. Rev Environ Contam Toxicol 99: 1-46.
- After 10 y, expect no more than 0.3 % of original body burden to remain in fish

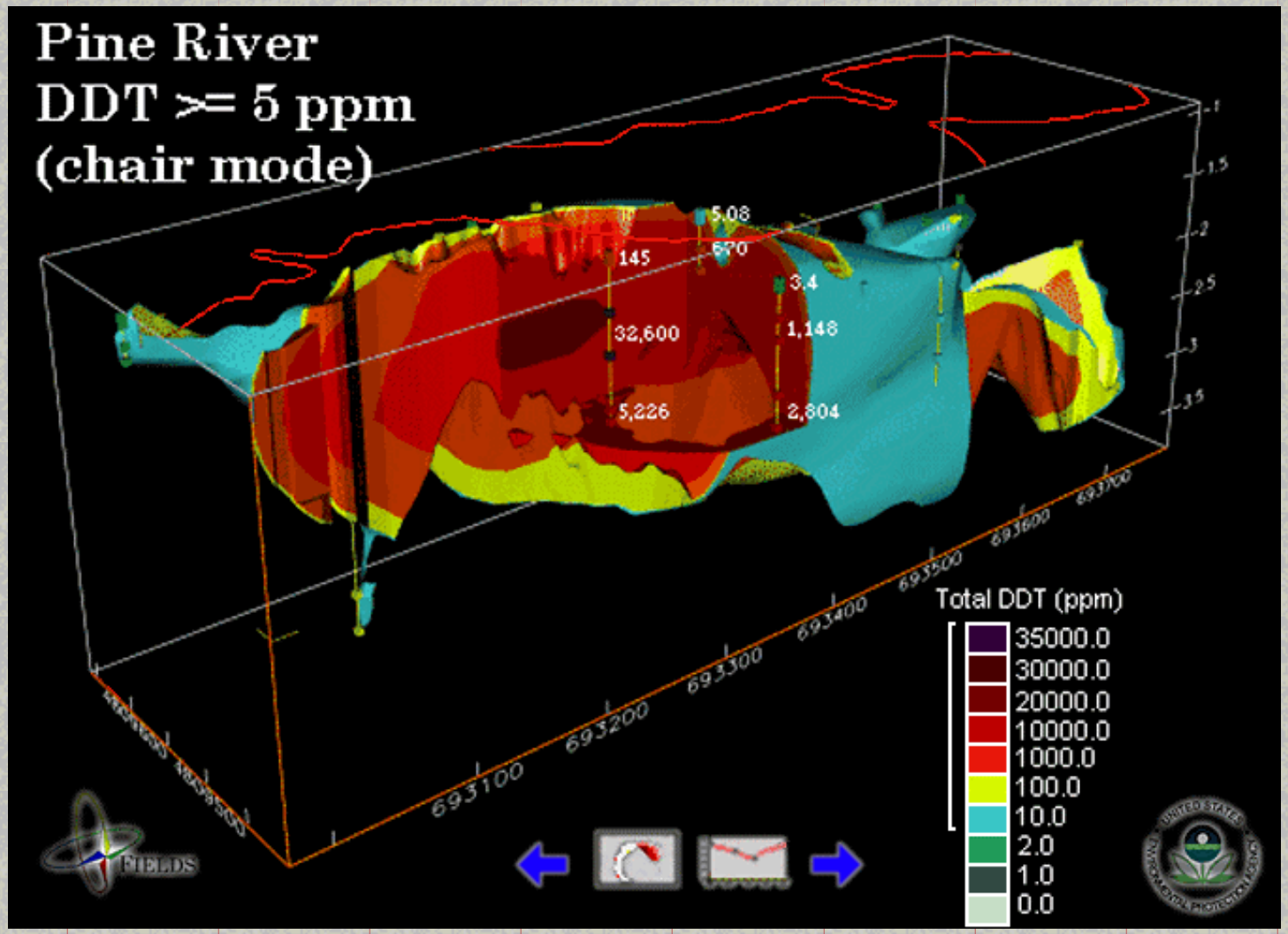
Response to Nonattenuation

- 1997 – sediment/fish investigations
- 1998 – risk assessments of sediment contaminants (HH and wildlife)
  - Main contaminant of concern - DDT
- 1999 – sediment removal action
- 2000 – sediment remedial action (ongoing)

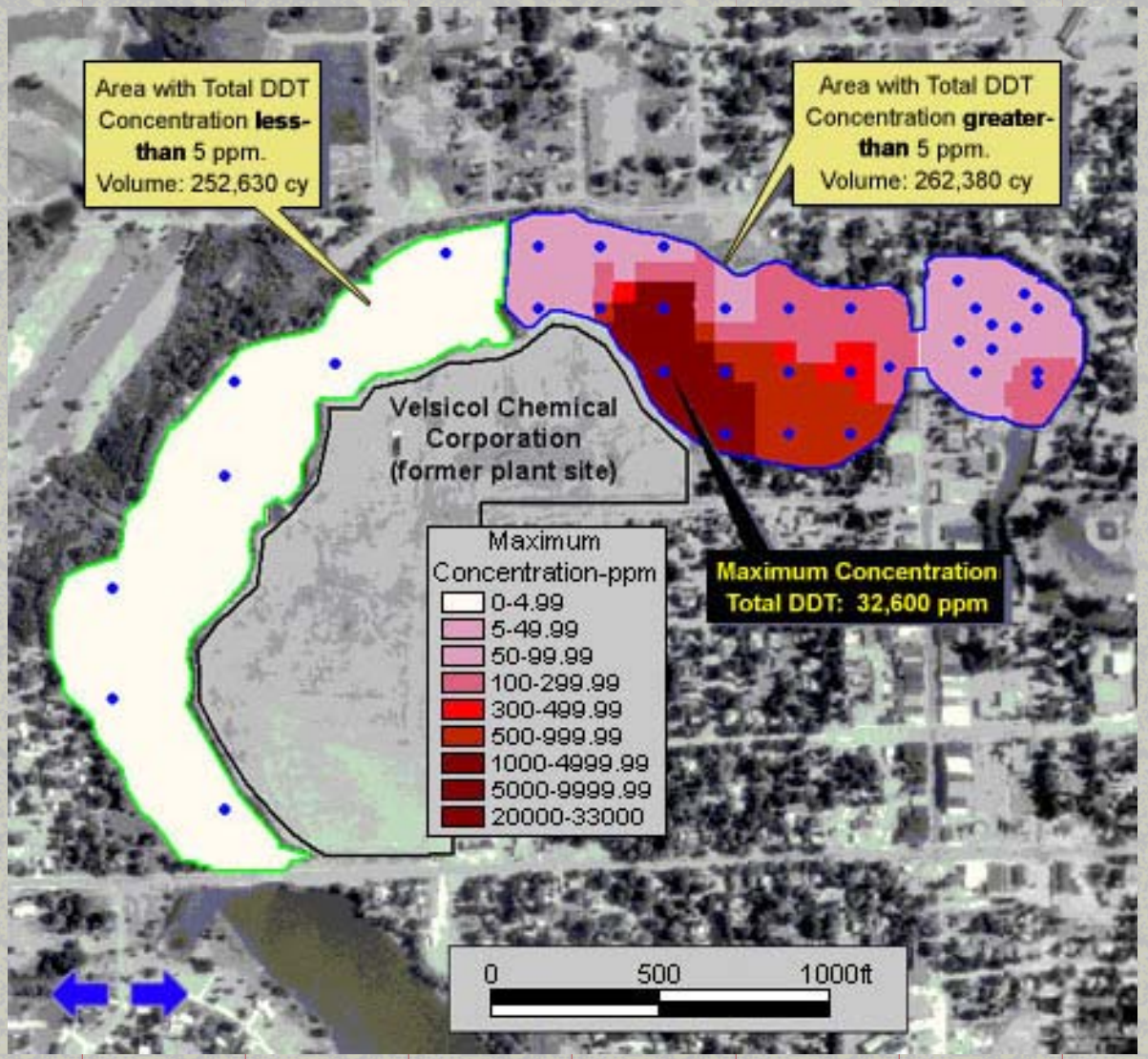
Sediment Sample Locations



3-D Sediment DDT



Sediment DDT Distribution



Why Did Attenuation Fail?

- Location of contaminated sediments behind dam appears favorable for natural “capping”
  - (but not for attenuation by erosion)
- The reasons why natural processes failed to attenuate contamination at this site are not fully understood.

Why Did Attenuation Fail?

- Potential explanations
  - river characteristics
  - co-contaminant effect on bioavailability
  - biotic effects
  - incomplete source control

River Characteristics

- Insufficient natural “capping”
  - 15 years after consent judgment
- 1997 surficial sediment sampling in St. Louis Impoundment (0-6 inch)
  - 68 % with >0.8 ppm DDTR (21/31)
- Middle basin (received plant discharge)
  - 34 ppm DDTR mean surficial conc.
  - 169 ppm DDTR maximum surficial conc.

River Characteristics

- Low sediment loading?
  - Relatively short reach (2.5 river miles) to next upstream dam (Alma, MI)
  - Only 2 relatively small tributaries (Horse and Sugar Creeks) in this reach
- St. Louis dam prevents major scouring losses of contaminated sediments

Co-contaminant Effects

- Upstream source of petroleum wastes (refinery at Alma, MI)
  - Co-mingled with Velsicol wastes in St. Louis Impoundment sediments
  - Sediments appear dark and oily, and have a strong petroleum odor
  - Except in areas of highest DDT conc. (at percent levels), which are white

Co-contaminant Effects

- Effect of petroleum products on partitioning of nonionic organics depends on the petroleum viscosity
  - Affects oil sorption vs. emulsion components
  - High viscosity oily wastes – decreased partitioning of co-contaminants to water
  - Low viscosity – increased partitioning
    - Walter, T., et al. 2000. Chemosphere 41: 387-397.

Biotic effects

- Carp bodywt increased during monitoring
  - Impoundment
    - 1989 1.1 kg
    - 1995 1.8 kg
    - 1997 3.1 kg
  - Downstream of dam
    - 1985 1.2 kg
    - 1994 2.0 kg
    - 1997 2.8 kg

Biotic Effects

- Impaired reproduction?
  - 9-15 y usual longevity for carp (47 y max.)
    - Brown, M. 1957. The Physiology of Fishes, Vol. 1. Acad. Press. pp. 361-400.
  - Increased size over monitoring period might reflect non-reproducing population
- Embryo/yolk-sac fry more susceptible to DDTR lethality than fry or juveniles
  - Carlson, D., et al. 2000. EHP 108: 249-255

Incomplete Source Control

- Impoundment surface water
  - 0.1-0.3 ug/L DDTR (1999) (excluding dewatered Removal sediment area)
- Groundwater at site near Impoundment
  - 0.1-2.0 ug/L DDTR, mean 0.7 ug/L (2000)
- Stained soils observed between slurry wall and river during removal excavation
  - DDTR conc. in seep 54,700 ug/L (2000)

Containment Assessment

- 94 % of average flow through the containment system passes through underlying clay till
  - 9.7 million gal/y (1984-1996)
- 6 % through containment wall
  - 0.6 million gal/y (1984-1996)
    - Estimates by Memphis Environ. Center prepared for Velsicol Chemical Corp. (1997)

Containment Assessment

- Monitoring wells along Impoundment
  - 0.69 ug/L DDTR (0.14-2.0 ug/L) (2000)
  - 0.025-0.073 kg/y to river (mean-max.)
    - assuming 100 % delivery to river
- Mean release of DDTR to Impoundment surface water is 30 kg/y
    - based on 1999 surface water measurements excluding dewatered Removal sediment area
- Groundwater contribution only 1-2 %

Containment Assessment

- Assume all flow through containment wall is at seep concentration:
  - 54,700 ug/L DDTR (2000) (single analysis)
  - 128 kg/y DDTR to river
- Exceeds loading to river based on surface water measurements (30 kg/y)
  - excluding dewatered Removal sediment area

Seep Contribution Issues

- Problem – contaminated fill was used outside of containment wall
  - Seep measurement might represent localized (not general) contamination
  - Seep conc. (57,700 ug/L) is 2-3 orders of magnitude > solubility
    - 25-140 ug/L at 25 ^{o}C (pp-/op-DDT, DDE, DDD)
- Ongoing investigation

Summary

- Even in a low-energy environment behind a dam, natural processes were insufficient for reducing risks related to sediment DDT contamination within an acceptable time-frame in the Pine River.
  - High surficial sediment DDTR levels after 15 years
  - No decrease in fish tissue DDTR levels over the last decade

Summary

- Discharge of contaminated groundwater to the Pine River can be eliminated as a possible cause of nonattenuation.
- Potential responsible factors include
  - Low sediment loading/lack of scouring
  - Co-contaminant effects on partitioning
  - Increased mean fish size over time
  - Poor containment wall performance

Summary

- The effectiveness of natural process remedies may be constrained by a variety of abiotic and biotic processes.